SUMMARY REPORT

on

A SEARCH FOR NEW RESISTIVE MATERIALS FOR HIGH-STABILITY, HIGH-TEMPERATURE-OPERATING RESISTORS

to

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by

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SUMMARY

This report summarizes the work on the development of a new resistive material during the period of November 8, 1949, to December 8, 1953.

The specific aim is to develop a resistive material which has good resistance stability at operating temperatures of 200 C, has a low temperature coefficient of resistance (TC), and covers the resistance range of 10 ohms to 10 megohms.

The classes of materials surveyed to meet the above requirements were the borides, carbides, nitrides, and silicides of the transition elements in the third, fourth, and fifth groups of the periodic table. Materials of these groups were fabricated and tested for electrical conduction, high-temperature resistance stability, and range of TC. On the basis of these tests, materials were compared and either classed as suitable for development or undesirable for this application.

The first section of this report covers the comparative evaluation of the resistance stability and TC of all the materials considered. Three materials, Cr-N, Cr-Si, and Cr-Ti-N, were selected for further study. In the second section, the information obtained from the further study of Cr-N and Cr-Si materials is presented. The outstanding possibilities of the Cr-N material are pointed out, along with the problems present in producing a low TC film. The Cr-Si has shown good oxidation resistance, but production of homogeneous material has not been obtained. Fabrication by thermal evaporation is now under study. The third section shows the development of a Cr-Ti-N resistor utilizing Cr-Ti-N film material. The fourth and final section indicates the nature of future work.

INTRODUCTION

In the electronic-component field, there exists the need for a fixed resistor which can operate up to 200 C with a small resistance change and also can cover the resistance range of 10 ohms to 10 megohms. In order to meet the low-resistance-change requirement, the material used in the

resistive component must have two characteristics; first, the permanent resistance change due to environmental operating conditions must be less than several per cent, and second, the TC must be less than 100 ppm/C (parts per million per degree centigrade).

The need for this resistor exists because of the inability of present resistors to meet these requirements. Composition resistors have neither the stability nor the TC to be usable. Special alloy wire-wound resistors have good TC and stability characteristics. However, because of the cross-section limit to which the wire can be drawn and the low value of the wire resistivity, high-resistance resistors cannot be made in small sizes. Film-type materials are the logical next step. In the case of the carbon and borocarbon film resistors, operation at 200 C is only possible with an elaborate protective coating. Also, for operation between -65 and 200 C, their TC of 500 ppm/C (for high-resistance films) gives them a resistance change of 10 per cent at the 200 C temperature. This is outside the low-resistance-change requirement. Commercially available noble-metal film resistors are the same in this respect, since in order to cover the range of 10 ohms to 10 megohms, the TC varies from approximately 300 ppm/C to -500 ppm/C. The tin oxide film resistor is satisfactory as far as the resistance stability is concerned. However, the maximum resistance available at a low TC is less than 1/4 megohm. For these reasons, these materials have shortcomings which keep them from being used in the present application.

SECTION I. SURVEY OF THE ELECTRICAL PROPERTIES OF CERTAIN MATERIALS TO DETERMINE THOSE DESIRABLE FOR USE IN HIGH-STABILITY, HIGH-TEMPERATURE-OPERATING, HIGH-RESISTANCE-RANGE RESISTORS

In conducting a survey of this type, the phases to be considered are:

(1) The specific properties a material must have to qualify for use in this application.
(2) The method of selecting which materials are to be considered.
(3) The preparation of the materials selected for consideration.
(4) The measurement of the properties of those materials that can be prepared.
(5) The comparison of the resistive material properties and the selection of those which look to be most promising.

The Properties Required of Materials to Qualify for Use in This Application

In order to evaluate the quality of a material, it is necessary to compare its properties to those desired in the acceptable unit. The required properties are:

(1) A permanent change of resistance of less than several per cent while operating at 200 C ambient air temperature for 1000 hours.
(2) A TC of less than 100 ppm/C over the temperature range -65 to 200 C.
(3) A voltage coefficient of resistance of less than 0.02 per cent per degree centigrade over the rated continuous working voltage for each resistor.
(4) A resistance change of less than 5 per cent when subjected to variations in humidity while operating between -10 and 65 C for 240 hours.
(5) A stability comparable to that for tests listed above when subjected to temperature cycling, low-temperature exposure, short-time overload, and shelf-life tests.
(6) A resistivity so that the maximum physical size is near 1/4 inch in diameter and 1 inch long for a 1-watt resistor, and other sizes dependent on power ratings.
(7) The material must also have properties so that the final-resistor can be:
    (a) Capable of covering the resistance range from 10 ohms to 10 megohms.
    (b) Operate at full power rating anywhere between -65 and 200 C.

The Method of Selecting Materials to be Considered for the Survey

A summary of the specific properties as listed above shows that to be successful a material must roughly meet three requirements. It should have a low TC, a resistivity of about 10^{-2} ohm-cm, and excellent stability while operating between -65 and 200 C. From a group of articles in the literature, resistivity and TC data were obtained for materials from metals to insulators. A graph of these data indicated that materials with resistivities between 10^{-4} ohm-cm and 10^{-2} ohm-cm should exhibit low TC's. Also, it was found that, in general, compounds formed from the transition metals and boron, carbon, nitrogen, or silicon had resistivities in this range. It seemed likely that several of these refractory compounds, i.e., the borides, carbides, nitrides, and silicides might simultaneously meet the TC, resistivity, and stability requirements. Therefore, these groups of compounds were selected for the survey.

Principles of Several Methods of Preparation of Electrical-Resistance Materials

There are several important factors which must be considered in the preparation of a resistive material. These are (1) the physical size and particular geometry, (2) the choice of support material if the resistive material is not self-supporting, (3) the type and control of material-formation processes, and (4) the ease of production.

As stated previously, the resistivity of the final material will probably be in the range 10^{-4} to 10^{-2} ohm-cm. In order to obtain high-resistance-value resistors, using materials with this resistivity, it is necessary that the cross-sectional area of the final resistor be small. Therefore, the resistive material is fabricated in thin film form on the surface of a cylindrical base and then further decreased in cross section by the technique of spiralling.

Because of the high temperatures necessary for the formation of the compounds to be studied, the base materials must be of the high-temperature-ceramic type.

Information from literature and experience was available on the formation of a number of the refractory compounds. Most of this information pertained to bulk material. Several methods of preparation were investigated to form these compounds successfully in filmlike form. For clarity, the following definitions of the compound constituents will be adopted. Call the originally most metallic component of the compound, e.g., Zr or Cr, the metallic element, and call the less metallic component of the compound considered, e.g., N or Si, the metalloid component.

Vapor-Phase Decomposition

While enclosed in a gas-tight system, the base upon which the resistive material is to be deposited is heated to a high temperature. The enclosure is then flushed with an inert gas. Subsequently, hydrogen gas is bubbled through or passed over a halide of the metallic element, and also through a halide of the metalloid element. Vapors of both these solutions are carried into the reaction zone, and, under the conditions of high temperature and presence of a reducing gas, the decomposition of the halides takes place. With the proper conditions, the metal-metalloid compound may also be formed upon the base. The base and compound are then cooled to room temperature and removed from the enclosure.

The deposition of only the metallic element on the base rod also can be accomplished with this method. In this case, the carrier gas (hydrogen) introduces only the halide of the metallic element. The metal-coated rod is

then converted to the desired compound by processing similar to that used for the conversion of evaporated metal films, covered in the next section.

Evaporation Conversion

In the evaporation-conversion method, the metallic element of the compound to be formed is deposited on the base material by thermal evaporation. Specifically, while under vacuum conditions, a sample of the material to be deposited is heated until rapid vaporization occurs. The base is placed close enough to this source so that the vaporized particles can travel to and condense on this base. In some cases, indirect heating of the source with an electrically heated boat material was used; whereas, in others, electric-arc heating was employed. The metal film and base are then raised to the metal-metalloid reaction temperature and exposed to a gas containing the metalloid component. When the conditions are favorable, a reaction between the two materials occurs and the compound should be formed. The base and compound are then cooled to room temperature.

Sintering

The metallic constituent of the compound is applied to the base material by brushing on a mixture of the metal powder and a binder liquid. The binder is baked off by firing the base and liquid coating at high temperatures in the presence of hydrogen gas. The resulting sintered metal film is then converted to one of the compounds by high-temperature exposure to the proper metalloid-containing halide gas.

In general, these are the methods which have been used to prepare the bulk of the compounds included in the survey. Several other methods have been used or examined in connection with the preparation of specific compounds. They shall be described when the particular material is discussed.

The remaining point to be considered in the preparation of materials is the ease of production. This consideration is of importance in deciding whether a material can be carried through the development stage. Generalities cannot be set down; therefore, each case is decided on an individual basis.

The Oxidation-Resistance and TC Evaluation

As has been mentioned previously, the borides, carbides, nitrides, and silicides of (1) the transition elements in the third, fourth, and fifth groups of the periodic table, (2) iron, cobalt, and nickel, and (3) some alloys were to be investigated. In general, the evaluation progressed in three phases:

(1) Phase one consisted of the determination of the relative oxidation resistance and TC for those materials in the whole group which had resistivities in the proper range.
(2) In phase two, ten of the original group of about 60 compounds were selected for a more definitive study of their TC, oxidation resistance, and several other electrical-stability properties.
(3) Phase three included the development of the most promising materials, i.e., the nitrides and silicides of chromium and certain chromium alloys.

The above program was carried out during the four years of the project. However, the research did not exactly follow this order. That is, the emphasis on certain materials may have changed during the program dependent upon the results obtained on related materials. In some cases, the investigations did not proceed beyond the literature phase. In others, they were carried through the materials preparation stage and further work stopped because of the inability to prepare the material in film form. Many materials were carried through the complete evaluation. The results of the first phase are given in the next paragraphs.

The borides of Ti, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, W, Cr-Co, and Cr-Ti were investigated. In general, the boride production was difficult to control. The reaction to produce the boride was extremely dependent on purity of the gas; small water or oxygen contaminations resulted in powder formation. Of those materials successfully formed, several were nonconducting; some were nonconducting until thick layers had been built up, and several had poor oxidation resistance. Two materials, Mo-B and Ta-B, were selected for further study.

The carbides of Ti, Cr, Mn, Fe, Co, Ni, Nb, Mo, Ta, and W were investigated. Several of those, Mn-C, Fe-C, Co-C, and Ni-C, are known to be unstable. Some could not be formed. The literature showed that, in many cases, the temperature of formation of the carbides exists above the practical limits imposed by the base and the production apparatus. Also, unless highly specialized process controls are invoked, incomplete carburization, or the deposition of free carbon, may occur. Mo-C films were successfully prepared and, although originally considered for further study, no further work on them nor any of the carbides was done.

The nitrides of Mg, Ti, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Ta, W, and Cr-Ti were investigated. Several of these could not be prepared in film form; some which could be formed were not conducting. It is worth noting that the nitride films were more easily prepared than any other type. In no cases were the films powdery or nonadherent. Five of the nitrides had poor oxidation resistance. The nitrides of Ti, Cr, and Cr-Ti were selected for further study.

The silicides of Mg, Ti, Cr, Mn, Fe, Co, Ni, Zr, Nb, Mo, Ta, W, Cr-Fe, Cr-Co, Cr-Ni, Mn-Fe, Mo-W, Mo-Ta, Ta-W, Cr-Ti, and Cr-Pt were investigated. There was difficulty in preparing homogeneous materials. As in the case of the borides, good film preparation resulted only in the absence of the oxidizing contaminants. Four of this group seemed to exhibit jumpy, intermittent resistance changes, and five had poor oxidation resistance. A few had acceptable oxidation resistance but also had a large positive TC. Those worthy of further study were Cr-Si, Cr-Co-Si, Mo-Si, Ta-Si, and W-Si.

On the basis of these comparative standings in the oxidation-resistance and TC tests, the second phase consisted of the more extensive study of the properties of Mo-B, Ta-B, Ti-N, Cr-N, Cr-Ti-N, Cr-Si, Cr-Co-Si, Mo-Si, Ta-Si, and W-Si. Additional test facilities were set up to study such characteristics as: (1) the resistance stability when subjected to 1000-hour exposures at 200 C ambient air temperatures, (2) TC between -65 and 200 C, (3) resistance per square, (4) voltage coefficient of resistance between one-tenth and the full-rated continuous working voltage for each unit, (5) cycled-load high-humidity tests, and (6) short-time overload. In the preliminary survey, the electrical-characteristic comparisons were made relative to each other and the best compounds selected on this basis. During the second phase, the test measurements were of an absolute nature, and the values compared with the required characteristics, given at the beginning of this section.

The testing of these materials showed the following results. Under a 200 C ambient air temperature, 1000-hour life test, both the Mo-B and Ta-B films exhibited permanent resistance changes larger than 25 per cent. Also, their temperature coefficients of resistance were not inherently low; therefore, these materials were eliminated from further study.

Further attempts to produce W-Si films resulted in films which, in many cases, exhibited jumpy, intermittent resistance changes during resistance measurement. No advantages over the silicides of molybdenum or chromium alloys were observed; therefore, work on W-Si was discontinued.

Ti-N films exhibited changes in accelerated no-load aging tests which were higher than those exhibited by Cr-Ti-N resistors. Films with TC's in the desired range of less than 100 parts per million could not be produced at resistances above 150 ohms per square. Since the films showed no advantages over the nitrides of chromium or Cr-Ti, further work on Ti-N was discontinued.

The resistance increases exhibited by Cr-N, Cr-Ti-N, Cr-Si, Cr-Co-Si, Mo-Si, and Ta-Si were between 5 and 20 per cent for the 1000-hour life test at 200 C. In the case of the silicides, one problem which existed was in the production of films of homogeneous material. Neither the vapor-phase-decomposition, the evaporation-conversion, nor the

sintering methods gave desirable results. Relatively speaking, the Cr-Si and Cr-Co-Si are the better materials of the silicides, since they are easier to produce and the cost of the materials is less. However, until the practical difficulty of producing acceptable materials can be solved, the development of all silicides has been set aside. However, as will be reported later, the development of the Cr-Si film has been reopened, contingent upon the success of the formation of this material, utilizing deposition by special thermal-evaporation techniques.

The Cr-N and Cr-Ti-N compounds showed the most promise. Developmental work has been carried forth on them during phase three of the program. The specific accomplishments are summarized in Section II and Section III below.

SECTION II. FURTHER STUDY OF THE ELECTRICAL PROPERTIES AND STABILITY OF Cr-N AND Cr-Si FILM MATERIALS

The Cr-N and Cr-Ti-N film materials have the most promise of being produced for high-stability high-operating-temperature high-resistance-range resistors. If it can be fabricated, Cr-Si should also prove to be a good material. The Cr-Ti-N material has been taken through the developmental stage, and methods of producing a resistor of this material on a production basis are being examined. The development from the prospective film to fabricated resistor stage is covered in Section III of this report. The intensified study of the properties of Cr-N showed that this film has the greatest potential of any of the materials studied. However, because of the extreme sensitivity of the temperature coefficient of resistance to the film chemical and physical properties, the development has not proceeded as rapidly as has that of the Cr-Ti-N. The Cr-N properties and important production factors can be summarized in several paragraphs.

Electrical Properties of Cr-N

While operating under conditions of the 1000-hour 200 C life test, the majority of the Cr-N films exhibit permanent resistance changes of between 5 and 20 per cent. In isolated cases, a change of less than 5 per cent has been measured. The particular value is a function of the film thickness, and, as for all film-type resistive elements, the change is sensitive to base-surface irregularities.

It is possible to make films with TC's between -4000 ppm/C and +3000 ppm/C by nitriding at any single temperature between 900 and 1200 C. The particular value of the TC for a given nitriding temperature is dependent

upon the thickness of the initial chromium film. Also, it is found that the relationship between the TC and the resistance per square (equal to the resistivity divided by the thickness) is dependent on the nitriding temperature. Specifically, the value of the resistance per square at zero temperature coefficient is different for different nitriding temperatures. Thus, by varying film thickness and nitriding temperature, films of different resistance per square, with low TC's, can be made. The data so far have shown that values of resistances at low TC's vary from 50 to several thousand ohms per square. Therefore, with this range, and by utilizing the resistor spiralling technique, low temperature coefficient of resistance resistors with values between 10^2 and 10^7 ohms are possible.

The voltage coefficient of resistance of Cr-N is less than 0.02 per cent/volt for voltages up to the rated continuous working voltage for each unit.

Other test results have shown changes of less than 3 per cent for a 300-hour exposure under the conditions of 95 per cent relative humidity, cycled d-c load, and 75 C ambient; changes of less than 1.0 per cent were due to repeated temperature cycling between -65 and 200 C; and changes of less than 0.4 per cent were due to 250 per cent 5-second-duration overload voltage.

Methods Used to Prepare Cr-N

Single and combination methods have been studied for the preparation of Cr-N. These include vapor-phase-decomposition, "paint", sintering, carbonyl, and evaporation-conversion processes.

The principles of the vapor-phase-decomposition, evaporation-conversion, and sintering methods have been presented in Section I of this report. The paint process consists of applying, either by brushing or dipping, a layer of chromium chloride to a base material. The painted base is then nitrided in an NH_3 atmosphere at temperatures in the range 900 to 1200 C, the specific temperature being dependent upon the particular electrical film properties desired. In the carbonyl process, the initial chromium film is deposited on the base material by the thermal decomposition of a chromium carbonyl. This metal film is then nitrided at temperatures between 900 and 1200 C. The literature pertaining to this method showed that the deposition of chromium was more difficult than the deposition of either molybdenum or tungsten, both of which required elaborate controls for uniform film deposition. Therefore, no experimental work was done using this method. In all except the evaporation-conversion method, the control of thickness in the region below 1000 A is poor. Since it is necessary to be able to closely control the absolute thickness and thickness uniformity in order to determine the properties of Cr-N, further developmental work on this material was done with films made by the evaporation-conversion method.

The essential steps in the present usage of the evaporation-conversion method are as follows. A film of chromium metal is deposited on a ceramic base by thermal evaporation in vacuum. For convenience in spiralling, the base is cylindrical in shape, and the materials which have been found most suitable are either zircons or aluminas. Although bases made from either of these materials seem to be chemically inert at the high nitriding temperature, the practical problem of base fabrication without surface irregularities is a function of the manufacturer's production equipment. The film and base are then exposed to an ammonia atmosphere at temperatures between 900 and 1200 C. During this exposure, the chromium film is converted to a chromium nitride compound. The nitride film and base are then cooled to room temperature.

The thickness of the final nitride film is determined by the amount of chromium film originally deposited on the ceramic base. By using a weighed charge of powdered chromium for a source and a known and reproducible evaporating geometry in the evaporation step, chromium films of desired thicknesses can be produced. After these have been nitrided, the electrical properties of the nitride film can be correlated with one of its physical properties, the thickness, by virtue of the known conditions used to evaporate the initial chromium film. In this way, films of preferred electrical properties may be reproduced.

Problems to be Studied for the Complete Evaluation of the Cr-N Material

The properties of the Cr-N material have shown it to have the potentialities necessary for use in a high-stability, high-temperature-operating, high-resistance-range resistor. However, certain of the processing conditions need further refinement before low-TC films can be produced practicably. The most important of these are the obtaining of base materials which are simultaneously free from microscopic surface irregularities and chemically inert at temperatures up to 1200 C, the control of thickness of the initial chromium film, and the fine control of nitride-film composition. Each of these problems is being studied so that the potentialities of the Cr-N material may become the reality of a Cr-N resistor.

Investigation of the Production of Cr-Si by Thermal-Evaporation Methods

The silicides of Cr, Mo, Ta, and W have shown themselves to have good oxidation properties. However, the production of these materials by the evaporation-conversion and the vapor-phase-decomposition methods proved to be unsatisfactory. This resulted because the desired homogeneity and composition could not be controlled, since both solid silicon and the

metallic element were capable of existing independently in film form in the temperature range of deposition which was studied. A few silicides were made by the sintering process, but insufficient bonding within the films and to the base was obtained. Therefore, the sintering process also was considered unsatisfactory. For these reasons, the production of the silicides was set aside. Recently, it was decided to attempt the production of the Cr-Si material utilizing special evaporation techniques. One of these techniques is the dropped-powder hot-boat method. Under vacuum conditions, mixed powders of chromium and silicon are dropped from a hopper onto an evaporation boat held at about 2000 C. This temperature is high enough to bring about the instantaneous evaporation of both components. Any film deposited on a backing placed in the region of the source will then be a mixture of the two materials being evaporated. The properties of the films as deposited, and perhaps subsequently heat treated, are to be investigated in order to evaluate the effectiveness of the formation of silicide compounds by this method. A number of films have been produced by the use of this method, but because of their electrical characteristics, there is some doubt as to the homogeneity of the material deposited. Further studies need to be made.

SECTION III. DEVELOPMENT OF A COMPLETED RESISTOR UTILIZING THE Cr-Ti-N FILM MATERIAL

The initial survey and further study showed that, considering both property characteristics and ease of production, the Cr-Ti-N material was the most desirable as a resistor material. Its only shortcoming seems to be its inability to cover the high end of the complete resistance range of 10 ohms to 10 megohms. It can successfully cover the range from 10 ohms to 0.5 megohm. Since it does seem to fulfill every other requirement, it had been considered worth while to develop a Cr-Ti-N resistor by using the Cr-Ti-N film material. This work has been carried through the measurement of the material characteristics and improvements in control of property reproducibility. In addition, the future plans include the evaluation of various methods of increasing the production of finished units. More extensive testing can then be performed on larger lots of these resistors.

Electrical Properties of Cr-Ti-N Films

The resistance stability for 1000 hours of operation at 200 C ambient air temperatures for unprotected Cr-Ti-N resistors is given in the following tabulation:

Resistance per Square, ohms	Stability at No Load, %	Stability When Loaded, %
>500	10 to 40	Insufficient data
<500	2 to 25	5 to 25

The load or no-load condition refers to operation or nonoperation at the rated continuous working voltage. The tabulated values are the per cent of increase from an initial value. The range of values is attributed to resistance changes not necessarily indicative of the characteristic stability of the Cr-Ti-N film material at the specified conditions, for instance, irregularities in the base give rise to hot spots in the film, and abnormal resistance increases are measured. Also, some of these films had baked silver contact bands which in some cases resulted in hot spots at the film-contact band junction. For these reasons, the minimum per cent change in each range is considered to be more characteristic of the material for the testing condition indicated. In the tabulation, the resistance per square difference separates the films into two thickness categories, those greater than 500 ohms per square are thin films, and those less than 500 ohms per square are thick films.

The tabulation shows three important facts. First, for loaded resistors, the absolute resistance change of about 5 per cent compares favorably with that of the stability desired in the ultimate material. Second, the permanent resistance change is dependent upon the extent to which the resistor is loaded. Actual film temperature measurements made on a loaded 1-watt resistor operating at 200 C ambient have shown that this change is due to the films being at about 220 C. The resistance change that results is comparable to that for a film operating at about 220 C ambient, with no load. Therefore this increased aging when loaded is due to increased film temperature rather than abnormal film behavior when under electrical load. The third point to notice is the dependence of the resistance increase on the thickness. Even though some of the resistors in the group with resistances per square larger than 500 ohms have acceptable TC's, the high permanent resistance change may prevent them from being acceptable.

In general, the TC varies from -200 ppm/C at about 1000 ohms per square to +200 ppm/C at 100 ohms per square. The resistance at the crossover from minus to plus TC is about several hundred ohms per square. With the controls now in use, the yield of films within the ±100 ppm/C range is about 60 per cent. The TC is a function of the thickness of the nitride film, but seems to be more insensitive to the nitriding temperature than it is for Cr-N films. This is true for temperatures between 1000 and 1200 C. Experimentally, it has been found that deviations from a mean in the TC versus resistance per square relationship can be decreased by giving the films a heat or conditioning treatment at elevated temperatures.

The voltage coefficient of resistance is less than 0.02 per cent/volt. This is for voltages up to the rated continuous working voltage of each unit.

When subjected to a humidity cycling treatment, the resistance of the Cr-Ti-N films increases between 3 and 13 per cent. For films protected with a silicone varnish, the increases are between 0.1 and 2 per cent.

A d-c overload test of 250 per cent applied for 5 seconds produced resistance changes of between 0.1 and 0.7 per cent.

Specific Description of the Processing of Cr-Ti-N Films

The composition of Cr-Ti-N material is a combination of chromium, titanium, and nitrogen. Two methods of producing the combination have been investigated. One was the paint process. Here, a dipping solution is made up of a chromium chloride hydrate and titanium chloride dissolved in ethyl alcohol with a small amount of ethyl cellulose as a binder. The ceramic base material is then immersed in this solution and withdrawn at a constant rate. The resulting coating is allowed to partially dry. The rod and film are then exposed to an NH_3 atmosphere at temperatures of about 1200 C. By using this method, conducting films which had fair properties could be produced. However, the property reproducibility was not good. This was traced to film discontinuities which were believed to occur because of the hydrolysis of the titanium. Therefore, this method of production was discontinued.

The second method is the evaporation-conversion production of Cr-Ti-N films. Essentially, this consists of depositing a layer of Cr-Ti on the surface of a suitable base material. The deposition is by thermal evaporation and condensation in vacuum. The Cr-Ti coated base is then exposed to an NH_3 atmosphere at temperatures of about 1200 C. Production of Cr-Ti-N films by this method has proven to be the most practical.

Base Material

There are two reasons why it is necessary to have a base material for the Cr-Ti-N film resistor. First of all, in the formation process, the film is built up from zero thickness. This dictates the need for a substrate material upon which to form the deposit. Secondly, with the thickness of material in use, the film is neither self-supporting nor strong enough to withstand handling. The base that is to be used must have the following characteristics:

(1) It must be relatively nonreactive with Cr, Ti, or NH_3 and have mechanical strength up to temperatures of 1200 to 1300 C.
(2) Be a good electrical insulator up to 200 C and/or 500 volts.
(3) Be able to withstand mechanical shock.
(4) Have its physical surface be free of irregularities such as cracks, marks, holes, or gouges, and it also must be nonporous.

To meet these requirements, ceramic materials such as glasses, porcelains, or sintered oxides must be used. Several representative samples of each of these groups have been tested, and rods composed mainly of either zircon or alumina have proven to be satisfactory. The Frenchtown zircon, No. 3569 has been used extensively with the Cr-Ti-N and satisfactorily meets the requirements set forth above.

In order to standardize procedures, each base rod is subject to a cleaning treatment before being coated by evaporation. The procedure consists of scrubbing with a hot detergent and rinsing successively with water then alcohol. This cleansing procedure is effective in removing surface contaminants deposited on the rods in handling after manufacturing.

Cr-Ti Metallic Coating

The base material described above is coated with a Cr-Ti metallic layer by condensation from a metallic vapor in vacuum. The facilities necessary for this production are (1) the source and method of obtaining the Cr-Ti vapor, (2) the positioning of the base material upon which the Cr-Ti is to be deposited, and (3) the provision of proper conditions for the evaporation and subsequent deposition of the Cr-Ti material.

Several methods of providing the Cr-Ti vapor have been utilized. The first is the vaporization of chunk pieces of Cr-Ti alloy. Pieces about 50 mm^3 were heated with a tungsten ribbon filament. Relative thicknesses of the deposit on the base rod were estimated from the length of time at a temperature high enough to produce vaporization of the alloy. A second method of achieving the Cr-Ti vapor is by dropping mixed powders of chromium and titanium upon an open tungsten boat held at about 2000 C. Most of the powders landing on the boat achieve sufficient thermal contact to vaporize. Others bounce from the boat because of either thermal or mechanical shock. Relative deposit thicknesses are estimated from the time a known amount of powder is dropped onto the boat. A third method is to evaporate a known weight of Cr-Ti alloy powder from a tungsten boat. All the powder in the boat is driven off. In this method, the relative thicknesses are determined from the weight of the charge evaporated. In general, the electrical characteristics of the final Cr-Ti-N resistors produced with any of these deposition methods are similar. It does seem though that films produced by the weight-loss method have poorer life stability than films produced by the other methods. However, this method gives the best thickness

control. Therefore, it is being developed and a study of the life-stability difference is being made.

Several aspects of the geometry between the vapor source and the condensing base material are important. In order to achieve maximum longitudinal-thickness uniformity, the source-to-rod distance should be large. On the other hand, because large charge weights are difficult to evaporate, closer distances are better. A workable condition has been reached at 7 cm. Since cylindrical bases are used, the easiest way to deposit uniformly on the entire outside surface of the cylinder is to situate the cylindrical axis of the rod perpendicular to a line joining the source and rod and rotate the base rod about this cylindrical axis. With straight rods and a true rotating mechanism, radial-thickness uniformity can be achieved with rod rotation speeds of 1000 rpm. Lower speeds may also be possible. Minimum rotation speeds have not as yet been established.

The condition which must be obtained for good evaporation and deposition is low residual air pressure. This feature decreases the oxidation of the vaporizing source material and gives vaporized-particle mean free paths long enough to allow use of convenient source-to-rod distances. Pressures between 10^{-5} and 10^{-4} mm Hg have been satisfactory.

Nitriding the Cr-Ti Coating

The nitriding can be described best by considering four topics: (1) the furnace to achieve temperatures between 800 and 1300 C, (2) the gas flow system, (3) the support used to introduce and hold the Cr-Ti coated base rod in the high-temperature reaction zone and gas-flow stream, and (4) the gas-temperature-time cycle through which the film and base are taken.

A furnace that has proved to be satisfactory is a quartz tube, surrounded by firebrick insulation and heated by Clobars between the insulation and quartz reaction tube. The temperature is automatically controlled with a thermocouple sensing element and a potentiometric controller.

The gas-flow system is composed of connection tubing, flowmeters, valves, rubber stoppers, the quartz reaction tube, and a gas-exit bubbler seal. The gases are commercial grade, helium is used for flushing, and ammonia is the reacting gas. The flow rate of each gas is monitored with individual silicone oil manometers. The exit bubbler contains mineral oil as the exit seal. The system operates with a pressure slightly higher than atmospheric.

The material of the support, or boat, for the introduction of the film and base to the nitriding zone must be nonreactive with Cr-Ti, zircon ceramic, or ammonia gas, at temperatures up to 1300 C. Also, the possibility of forming other contaminants which may be able to react with the Cr-Ti film must be minimized. Boats made from quartz have proved to be satisfactory.

The chronological gas-temperature-time cycling procedure for the Cr-Ti is as follows:

(1) Place resistor in boat and place boat in cold end of reaction tube.
(2) Secure reaction-tube fittings to a semitight system. Flush reaction tube with helium. Follow with NH_3 gas flush.
(3) When gas in reaction tube has been displaced with NH_3 gas, introduce boat and film to hot zone in reaction tube. Allow to remain for given time (usually 10 minutes). Withdraw boat and film to cold portion of reaction tube. Allow filmed base to partially cool in NH_3 gas. Flush reaction tube with helium and allow to cool further.
(4) When film and base are less than 100 C, open tube fittings and remove boat and film (5 minutes after withdrawal from nitriding zone).

Conditioning Treatment

The life testing of Cr-Ti-N films has shown that the permanent resistance increase as a function of time is rapid at the start. Then, after several hundred hours, it levels off to a smaller change. This suggests that the operating resistance stability may be increased by heat-treating the films at elevated temperatures before being put into use. This is called the conditioning treatment. It has also been found that when temperatures around 300 C are used for the conditioning, the scatter in the TC versus resistance per square characteristic is decreased. Preliminary results show that a 30-minute exposure at between 250 and 300 C has produced the desired result. When a larger number of resistors are made available by increased production, a more definite measure of the effectiveness of this conditioning treatment can be made.

Techniques Used or Developed to Transform the Cr-Ti-N Films Into Cr-Ti-N Resistors

The basic problem on this contract is the development of a new resistive material. However, in order to determine the effectiveness of a material in meeting the specified requirements, it is necessary to subject it, as a finished resistor, to simulated operating conditions, or to make certain measurements on the films which will be indicative of the film behavior under actual load-life tests, high-humidity tests, and temperature-cycling tests. This certain measurement might be of the change in resistance, or any other property, as a result of a special test (not an actual test condition) designed to produce an effect indicative of the actual film operating behavior. This method requires a knowledge of the relationship between the special test result and the actual film operating behavior. Since this knowledge is not now available, and since there have been only a small number of resistors

to test, the simulated-operating-condition test method was chosen for use. This choice necessitates the introduction of two resistor processing techniques, i.e., electroding and spiralling.

Electroding

In order to carry out the simulated operating condition tests, it is necessary to obtain electrical contact to the ends of the Cr-Ti-N film. This procedure is known as electroding. One of the standard methods of electroding film-type resistive elements is, first of all, to apply thick circumferential bands of a highly conducting material to each end of the filmed base. These bands may be applied by painting and heating, evaporation, chemical deposition, or electroplating. The second step in this process is to force small caps over each of these conducting bands. These are called end caps and have, as part of them, copper leads to which circuit connections can be soldered or clamped. The silver-plated-brass cap is of such a shape and size that, when it is forced over the band, film, and base, it makes a pressure contact and is held firmly connected to the contact band by the force fit. Because the end bands, end caps, and copper leads are of low resistance and are in intimate contact with each other and the resistance film, the resistance of the complete resistor is that due to the Cr-Ti-N film element.

Preliminary investigations of another contacting method, utilizing the contact band and a staked wire lead, did not produce satisfactory results. Here, a hollow cylindrical base is used, and the contact band extends around the end of the hollow cylindrical base. The copper lead is fixed to an end connector which is pressed into the inside of the hollow base. This decreases the diameter of the over-all unit. However, inherent problems existed; for example, this contact had poor mechanical strength, decreased contact area, and danger of damage to the relatively sharp exposed corners. Therefore, no further work was done on improvement of this design.

Until recently, the contact band was made from a commercial silver paint. This is a suspension of silver particles in a volatile binder. The mixture is brushed onto the surfaces to be covered and the binder removed by baking at elevated temperatures. The use of this end-contact material resulted in three disadvantages. First, as a result of either the silver, or the binder material, high-resistance junctions between the contact band and film sometimes formed. Failure resulted when the film at this junction became overheated and burned out. Second, since good electrical contact to the film is not made until after the band has been baked out at elevated temperatures, an unmeasurable resistance change was occurring during this bake period. This latter fact was verified when the present method of making the contact band was introduced. Third, high voltage coefficients of resistance were noted in some cases.

The present method of electroding is to use electroplated nickel end-contact bands and silver-plated-brass external end caps. The electroplated nickel bands provide a low-resistance, tightly bonded, high-stability contact. They are applied at room temperature and require no elevated-temperature baking period. The electroplating solution is a nickel strike bath. The nickel is electroplated over the Cr-Ti-N film for a length of 5 mm on each end. The end caps are then pressed over these nickel contact bands.

Spiralling

Spiralling is the operation whereby the resistance of a given area of film on a cylindrical rod is increased. The increase is caused by the simultaneous decrease in cross-sectional area and increase in length of the conducting path. In practice, a portion of the film on the cylindrical rod is removed in a helical path, the axis of which is coincident with the cylindrical-film axis. The removal of film is accomplished by grinding with an abrasive wheel. The helix is generated by rotating the resistor in a lathe chuck while the rotating abrasive wheel advances linearly along the lathe bed.

In addition to the resistance increase, the spiralling operation allows the testing of resistors in two additional ways. First of all, it is a measure of the uniformity of the film thickness. That is, if the film is not uniform, the TC of the spiralled resistor will be different from that of the unspiralled resistor. Secondly, the spiralling is helpful in detecting defects in the base material. If a portion of the cross-section of the conducting film is not present because of faulty film adherence or poor film formation due to base irregularities, the power dissipated in the missing area is increased. This gives rise to a hot spot and usually results in either an abnormal resistance increase or an actual open resistive element.

For a resistor 6 mm in diameter and about 20 mm long, spiralling has increased the resistance range at low TC from 100 to 1000 ohms to 100 to 500,000 ohms. To achieve this increase in resistance range, spiralling factors (the ratio of the spiralled to unspiralled resistance) between 5 and 2200 have been used.

Protective Coatings

It is known that an increase in stability and resistance to humidity effects can be improved by the addition of certain protective coatings on the film material. Also, some electrical-insulation protection is required on any resistor. Therefore, although the original intent on this contract was to exclude coatings which would protect against environmental conditions, the need for protective coatings was realized. Therefore, the program was altered to include evaluation of protective coatings which could be applied without elaborate or expensive additions to the resistor processing operations.

Silicone varnish, DC 996, was one of the first types studied. It was used both as a top coating on TiO_2 loaded polyterpene tung oil coatings and as a coating by itself. Some protection was offered by both uses, but further work was stopped on the polyterpene-type coating because of involved application methods. Other materials considered were a Teflon tape (heat cured and shrink fitted to the resistor), an epon resin, a polyester resin, and hermetic glass seals. Work on the first three of these materials was stopped after poor protection and thermal as well as flexural difficulties were introduced. The glass seals, which did indicate the beneficial effects of good protection on the Cr-Ti-N resistor, were not considered further because of their high cost. The silicones are easy to apply and offered protection. Therefore, varieties and modifications of this group were studied.

DC 935, because of its good temperature characteristics, particularly for the low end of the temperature range, was substituted for the DC 996. Loaded coatings were found to be better than the pure silicone. Loading materials that have been considered are powdered TiO_2, Al_2O_3, mica, and aluminum. The coating which seems to give the best protection consists of flake mica (150 mesh) in DC 935, applied in two coats on the resistors. In general, the permanent resistance change for these protected resistors is several times lower than that observed for unprotected resistors of comparable quality, composition, and thickness.

SECTION IV. CONCLUSIONS AND FUTURE PLANS

The results of the survey and developmental work have shown that three materials have properties which indicate they may qualify for use as high-stability, high-temperature-operating, high-resistance-range resistors. These are Cr-Si, Cr-N, and Cr-Ti-N. Each is at a different stage of examination.

Because of unfavorable production problems in the original investigation of Cr-Si, work on it was discontinued. Recently, consideration was given to the fabrication of films of this material using thermal evaporation in vacuum methods. Production of these films has not as yet been successful. However, because of the good oxidation properties of films that had been successfully produced, this year's plans include the continued investigation of the formation of Cr-Si films by vacuum-evaporation methods.

The Cr-N material shows properties indicative of an excellent resistive material. However, the attainment of the specific film characteristics which have low TC's is difficult. Therefore, the determination of whether or not low-TC Cr-N films can be practicably produced is now under study.

The Cr-Ti-N material has been successfully fabricated into resistors which meet most of the requirements set forth in the contract. The one limitation seems to be the maximum obtainable resistance of 0.5 megohm for films which have an acceptable stability requirement. However, it is hoped that either Cr-N or Cr-Si can be successfully made to cover the range from 1 megohm to 10 megohms. Future studies of the Cr-Ti-N resistors are concerned with the development and design of a prepilot-plant facility for the experimental production of a large number of Cr-Ti-N films and resistors.

Data for this report can be found in Battelle Laboratory Record Books Nos. 5068, pages 1-100; 5444, pages 1-100; 5684, pages 1-100; 6179, pages 1-28; 6698, pages 1-100; 7240, pages 1-100; 7740, pages 1-100; 8145, pages 1-100; 7847, pages 1-66; 8253, pages 1-2; 8448, pages 1-61; and 8537, pages 1-32.

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